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Elemental Analysis: CHNS/O characterization of rubbers and tires

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Keywords

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Goal

This application note reports data on CHNS/O determination on rubber and tire samples for quality control purposes, performed with the Flash*Smart* EA.

Introduction

Rubbers and tires are used in a variety of industries and for different final products. Rubber is the main raw material used in manufacturing tires, either natural or synthetic. Crude rubber is primarily hydrocarbon in nature and is thermoplastic. To eliminate undesirable properties such as malodorousness, rubber is treated with sulfur, accelerators, and also antioxidants which extend the life of rubber products by reducing the deterioration caused by atmospheric oxygen (or ozone). The other primary ingredient in tire rubber is carbon black, used to increase stiffness, tensile strength, and resistance to abrasion. Rigorous quality control begins with the suppliers of the raw materials. A tire manufacturer requires the raw materials to be quality tested before they are delivered to the plant.

One of the tests used in the production process is the determination of the elemental composition of rubber. Sulfur content is one of the most important parameters in the quality control of rubber products, as it is the main indicator of the sulfur blooming phenomena, which indicates the loss of quality of the tires.

For quality control purposes, the organic elements in rubbers need to be determined. For the determination of carbon, hydrogen, nitrogen, sulfur and oxygen, the combustion method is used.

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The Thermo Scientific™ Flash*Smart*™ Elemental Analyzer (Figure 1) allows the quantitative determination of carbon, hydrogen, nitrogen and oxygen in rubbers and tires. The Flash*Smart* EA based on the dynamic flash combustion of the sample, provides automated and simultaneous CHNS determination in a single analysis run and oxygen determination by pyrolysis in a second run.

This note presents data on CHNS/O determination in rubbers and tires to show the performance of the Flash*Smart* Elemental Analyzer.

Figure 1. Thermo Scientific Flash*Smart* Elemental Analyzer.

Methods

For CHNS determination the Flash*Smart* EA operates according to the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion reactor via the Thermo Scientific™ MAS Plus Autosampler with oxygen. After combustion the resultant gases are carried by a helium flow to a layer filled with copper, then swept through a GC column providing the separation of the combustion gases Finally, they are detected by a Thermal Conductivity Detector (TCD) (Figure 2). Total run time is less than 10 minutes. When using the NCS configuration, a trap filled with anhydrone was installed between the reactor and the GC column.

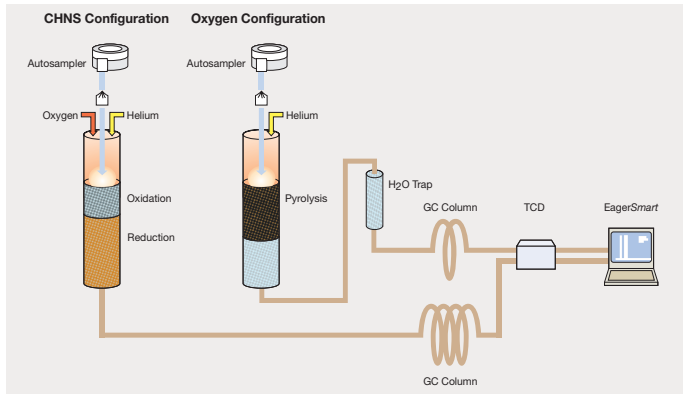

Figure 2. CHNS/O configuration.

For oxygen determination, the system operates in pyrolysis mode. Samples are weighed in silver containers and introduced into the pyrolysis chamber via the MAS Plus Autosampler or directly injected via the AI 1310 or AS 1310 Autosamplers. The reactor contains nickel coated carbon at 1060 °C. The oxygen in the sample, combined with the carbon, forms carbon monoxide which is then chromatographically separated from other products and detected by the TCD Detector (Figure 2).

A complete report is automatically generated by the Thermo Scientific™ Eager*Smart*™ Data Handling Software.

Figure 3 and 4 show the typical CHNS and oxygen chromatograms.

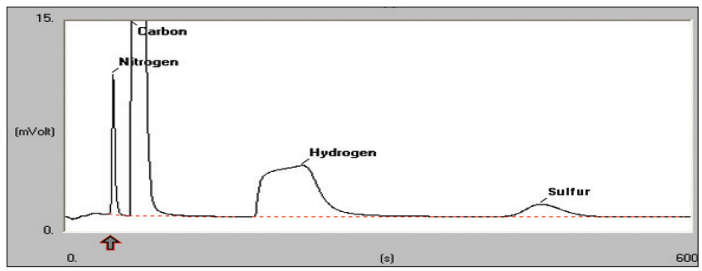

Figure 3. Typical CHNS chromatogram.

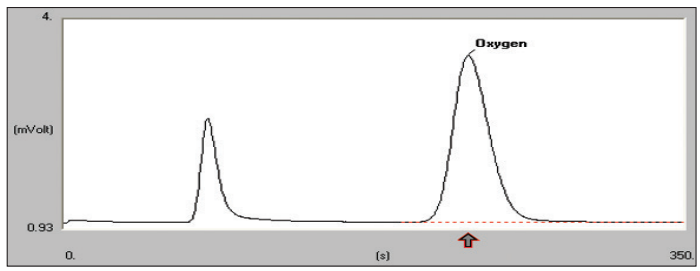

Figure 4. Typical oxygen chromatogram.

Results

Different rubber and tire samples were chosen to show the performance obtained with the system. The samples were analyzed without any pre-treatment, merely cut into small pieces for the analysis. For CHNS, NCS and sulfur only determination, the addition of Vanadium Pentoxide was used for a complete conversion of the sulfur. The sample was weighed at 2 – 3 mg.

For CHNS analysis the instrument was calibrated with BBOT* (6.51 N%, 72.53 C%, 6.09 H%, 7.44 S%) as standard using K factor as the calibration method. For oxygen analysis, Acetanilide (11.84 O%) was used as standard and the K factor as the calibration method.

** BBOT: 2.5-Bis (5-tert-butyl-benzoxazol-2-yl) thiophene*

Table 1. CHNS/O determination of rubber and tire samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%	O%	RSD%
Rubber 1	0.477 0.481 0.481	0.521	86.118 85.735 85.951	0.223	7.922 7.916 7.941	0.165	0.881 0.899 0.863	2.043	2.023 1.999	0.823
Rubber 2	0.336 0.321 0.325	2.420	86.560 86.233 86.329	0.195	7.719 7.674 7.707	0.303	0.639 0.634 0.658	1.967	1.932 1.904	1.010
Rubber 3	0.337 0.324 0.338	2.287	86.250 86.210 86.597	0.247	7.210 7.271 7.312	0.706	0.260 0.254 0.271	3.317	2.218 2.245	0.862
Tire 1	0.792 0.800 0.783	1.074	73.961 74.140 74.171	0.153	6.856 6.880 6.933	0.572	3.151 3.105 3.122	0.744	4.345 4.325 4.327	0.254
Tire 2	0.529 0.536	0.929	75.253 75.370	0.110	7.187 7.186	0.011	2.972 2.937	0.838	3.752 3.695 3.609	1.953
Tire 3	0.362 0.370	1.546	87.505 87.767	0.211	8.958 8.973	0.112	0.823 0.837	1.226	1.199 1.178 1.191	0.891

Table 2. CHNS determination of rubber and tire samples.

Sample	N%	RSD%	C%	RSD%	H%	RSD%	S%	RSD%
Rubber 4	0.628 0.636 0.633	0.666	82.447 82.272 82.104	0.208	11.279 11.300 11.298	0.1045	0.797 0.799 0.792	0.503
Rubber 5	0.625 0.616 0.623	0.790	82.210 82.661 83.161	0.576	11.263 11.114 11.366	1.123	1.095 1.015 1.033	3.989
Rubber 6	0.626 0.628 0.622	0.470	81.962 81.866 82.361	0.320	11.218 11.249 11.272	0.243	1.561 1.553 1.572	0.606
Tire 4	0.454 0.462	1.235	79.597 79.676	0.0701	6.945 6.937	0.0815	1.435 1.454	0.930
Tire 5	0.436 0.427	1.475	82.672 82.781	0.0932	7.137 7.137	0.000	1.666 1.668	0.0848

Table 1 shows CHNS/O data of different rubber and tire samples while Table 2 shows CHNS only determination of other types of rubber and tire materials. All data were obtained with a good reproducibility and no matrix effect was observed when changing the type of sample.

Table 3 shows the reproducibility of rubber samples analyzed using nitrogen, carbon and sulfur (NCS) configuration.

Table 3. NCS determination of rubber samples.

Sample	N%	RSD%	C%	RSD%	S%	RSD%
Rubber 7	0.277 0.280	0.737	85.802 85.503	0.247	0.927 0.936	0.751
Rubber 8	0.290 0.300	2.447	85.130 85.047	0.068	1.546 1.585	1.779
Rubber 9	0.293 0.293	2.477	84.881 84.751	0.108	1.969 1.934	1.268
Rubber 10	0.283 0.287	1.091	83.229 83.230	0.001	3.798 3.730	1.281

Table 4 shows the loss of sulfur value from the tire surface by analyzing its content in a new tire and a six month old tire. This effect is known as a sulfur blooming phenomena.

Table 5 shows the reproducibility of oxygen determination by pyrolysis of rubber samples.

Conclusions

The Thermo Scientific Flash*Smart* Elemental Analyzer allows the quantitative recovery of the elements from any matrix, with no memory effect when changing the sample.

The CHNS/O determination of tire and rubber samples is performed by the Flash*Smart* Elemental Analyzer without any pre-treatment of the sample.

The Flash*Smart* Elemental Analyzer meets laboratory requirements in terms of automation and high sample throughput. The Analyzer is modular and enables laboratories to perform CHNS determination in a single run and, with a configuration change, oxygen determination. Sulfur or nitrogen only analyses can also be performed, with a minor configuration upgrade.

Table 4. Sulfur blooming phenomenarequirements.

Sample	S% (new tires)	S% (six months old tires)
Tire A	2.605	2.484 – 2.499 – 2.487
Tire B	5.894	5.415 – 5.302 – 5.250

Table 5. Oxygen reproducibility of rubber samples.

Sample	O%	RSD%
Rubber A	2.176 2.181 2.174 2.171 2.181	0.186
Rubber B	1.825 1.819 1.837 1.810 1.810	0.622
Rubber C	2.122 2.115 2.117 2.130 2.114	0.303

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